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EXTRUSION MOLDING OF SORBENTS BASED ON SYNTHESIZED ZEOLITE

N. E. Gordina,[1] V. Yu. Prokof'ev,[1] and A. P. Il'in[1]

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The possibility of producing complex-profile thin-walled sorbents based on synthesized zeolite is investigated. It is proposed to use natural aluminosilicate as binders. Methods have been developed for controlling properties of zeolite-based molding mixtures by introducing a plasticizer or by alkali or acid modifying the binder structure.

Purification by sorption is finding increasing application in purifying sewage waste from cations of heavy metals. A promising material for producing sorbents is synthesized zeolite, whose specific chemical composition and crystalline lattice structure are responsible for its well-developed adsorption and ion-exchange properties [1, 2]. Such materials are industrially produced in the form of spheres of diameter 4 – 6 mm. One of the drawbacks of zeolite is the impossibility of its extrusion molding.

In turn, the production of sorbents of complex geometrical configurations with minimal hydraulic resistance is dictated by requirements on treating industrial sewage, in particular cleaning it from metal cations. Usually a flow subjected to purification moves by gravity, accordingly, the pressure differential in the sorbent layer should constitute fractions of an atmosphere. In order to ensure molding properties required for making sorbent of a complex geometric shape, it is necessary to add binding and plasticizing agents which are most frequently naturally aluminosilicates, since they are easily moldable, inexpensive, and available. The choice of aluminosilicates is also justified by the fact that these materials have sorption capacity with respect to metal cations. Furthermore, zeolite has a low crushing strength (2 – 4 MPa) and low abrasion resistance, which also justifies the introduction of a binder into the sorbent.

The sorption of metal cations from sewage is usually implemented using the sodium form of zeolite of the type A (NaA), which is determined by its specific structure [1].

The purpose of our study is to identify the composition of molding mixtures based on zeolite corresponding to the optimum parameters for extruding high-quality sorbents of a complex geometric shape, as well as issue recommendations on controlling the structural-mechanical and rheological properties of molding mixtures.

[1] Ivanovo State Chemical Engineering University, Ivanovo, Russia.

The initial material for preparing sorbents was zeolite NaA ($6Na_2O \cdot 6Al_2O_3 \cdot 12SiO_2 \cdot nH_2O$) produced by mechanochemical activation in a roller-ring vibratory mill [3]. Due to the abrasive effect of its milling bodies, in addition to milling, it is possible to significantly activate the material and thus to increase its sorption capacity due to the accumulation of various defects in the crystalline structure of zeolite and the increase in the number of Brensted acid centers on its surface. The binders for producing extruded sorbents based on zeolite were clay from the Malostupkinskoe deposit and kaolin from the Kyshtymskoe deposit that were introduced into molding mixtures by mixing with zeolite. The choice of this particular clay is due to the fact that this deposit is located in the Ivanovo Region (Kineshma District). Kyshtymskoe kaolin was chosen since it contains nearly 98% (here and elsewhere, wt.%) kaolinite and its located on the territory of Russia (Urals) [2]. Furthermore, to control the properties of molding mixtures, the clay before mixing with zeolite was treated in 10% HCl and 1-M solution of NaOH and also polyethylene oxide (PEO) was introduced as a plasticizing additive [4].

The structural-mechanical properties of molding mixtures were estimated based on the flow curves obtained with a plastometer designed by Tolstoy and processed using the Maxwell – Shvedova and Kelvin equations [5]. The flow properties were determined based on the full flow curves obtained with a Rheotest-2-50 Hz-Typ RV 2 rotational viscosimeter in the range of shear velocities of 5 – 4960 sec^{-1} [6].

The effect of the quantity of zeolite in a molding mixture on the extrusion of sorbents was studied for the zeolite NaA – Malostupkinskoe clay system (Fig. 1). The following regularity was established: with an increasing content of zeolite in molding mixtures, the share of plastic deformations decreases and the system passes to structural-mechanical types 0 and 3, which have prevalence of fast elastic deforma-

tions. Consequently, a decreasing quantity of clay leads to an excess of fast elastic deformations, which has a negative effect on the moldability of the mixture.

One of the methods for controlling the properties of molding mixtures based on zeolite involves introducing small quantities of surfactant agents, in our case PEO [4]. This makes it possible to control the molding properties of sorbents already at the stage of mixture preparation. The surfactants, which contain polar groups and nonpolar groups in the form of a carbon chain, being adsorbed on solvated clay particles become oriented in such a way that the polar groups are directed towards the dispersion phase and the nonpolar groups towards the disperse phase; with this the surface of the clay particles become hydrophobic, which increases the degree of dispersion of the material [4].

The additive of 1% PEO produces a less perceptible decrease in plastic deformation with a higher content of zeolite. Thus, the share of this kind of deformation in a system without surfactant additives and with 30% zeolite content is equal to 53%, whereas in the case of using PEO it is equal to 61%. Increasing zeolite content in the molding mixture to 70% without the surfactant additive decreases plastic deformation 2.4 times and with the additive decreases it 1.8 times. At the same time, the share of fast elastic deformations grows from 22 to 72% (without surfactant) and from 25 to 38% (1% PEO additive), i.e., in the first case it grows more than 3 times and in the second case it varies insignificantly.

The dependences of structural-mechanical constants on the content of zeolite in molding mixtures are similar both without the high-molecular surfactant, and in the presence of PEO (Fig. 2). The difference consists only in the absolute values of these parameters. Consequently, the type of the interaction of clay and zeolite with the dispersion medium has

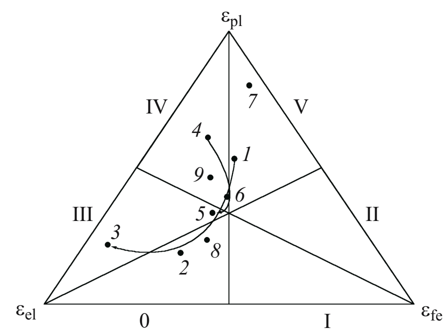

Fig. 1. Diagram of deformations in molding mixtures based on zeolite NaA and natural aluminosilicates: Zeolite content (%): *1*, *4*) 30; *2*, *5*) 50; *3*, *6*) 70. Content of PEO additive (%): *1* – *3*) 0; *4* – *6*) 1; *7*) 30 zeolite NaA + 70 Kyshtymskoe kaolin; *8*) 50 zeolite NaA + 50 clay treated with acid (10% HCl); *9*) 50 zeolite NaA + 50 clay treated in alkali (1 M NaOH).

the critical effect on structure formation processes in the considered systems, whereas PEO additives only provide corrections (sometimes substantial) to the structural-mechanical constants (Fig. 2 and Table 1).

It can be seen from Table 1 that as the content of zeolite structure increases, both in the absence and in the presence of surfactant, the plasticity of molding mixtures decreases from 7.50 to 0.91 and from 0.72 to 0.15 sec^{-1}, whereas the strength of the coagulation structure grows 4 and 2 times, respectively. At the same time, the relaxation period grows 4 and 3 times and the flow index grows from 0.24 to 0.63 and from 0.29 to 0.50. Such modifications impair the moldability of mixtures.

Note that when PEO additive is used, the molding mixtures have a stronger coagulation structure and lower relax-

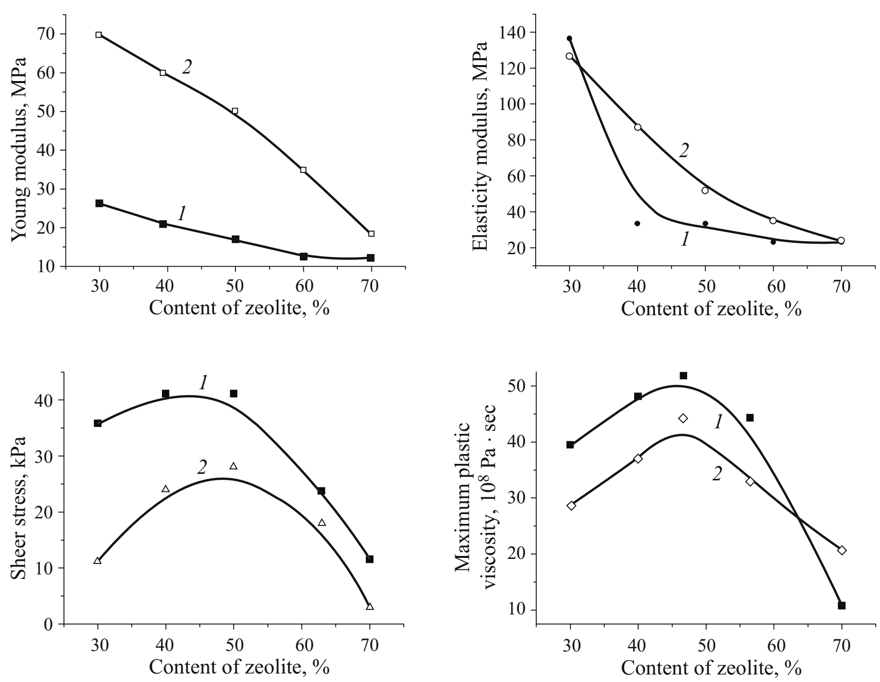

Fig. 2. Dependence of structural-mechanical constants on zeolite content in molding mixtures based on zeolite with Malostupkinskoe clay without additive (*1*) and with 1% PEO additive (*2*).

TABLE 1

Sample*	Zeolite content, %	Structural-mechanical properties		Rheological properties		
		plasticity, 10^{-6} sec^{-1}	relaxation period, sec	full flow power, MW/m^3	power on structure destruction, MW/m^3	flow index
Sorbent NaA + Malostupkinskoe clay (without surfactant)						
1	30	7.50	880	42.3	11.7	0.24
2	50	1.02	4250	19.4	3.9	0.61
3	70	0.91	3550	11.4	2.2	0.63
Sorbent NaA + Malostupkinskoe clay (1% PEO additive)						
4	30	0.72	1500	78.9	28.5	0.29
5	50	0.39	2000	56.9	14.4	0.30
6	70	0.15		34.2	8.7	0.50
Sorbent NaA + Kyshtymskoe kaolin						
7	30	16.0	250	22.3	5.4	0.56
Sorbent NaA + Malostupkinskoe clay modified with 10% HCl						
8	50	0.35	3240	29.3	4.5	0.49
Sorbent NaA + Malostupkinskoe clay modified with 1 M NaOH						
9	50	0.63	1145	39.7	12.2	0.30

* Numbers correspond to those shown in Fig. 1.

ation period values. The study of the effect of the type of binder on the properties of molding mixtures showed that when clay is replaced by kaolin, the share of plastic deformation sharply grows (1.5 times) and the relaxation time decreases (from 880 to 250 sec). All this causes a large number of defects in the course of molding, in particular, cord or "dragon tooth" defects. These processes can be attributed to different chemical compositions of the binders (Table 2). The data of x-ray structural analysis indicate that the main crystalline phase both in clay and in kaolin is kaolinite, which provides for considerable plastic properties. However, the clay contains significantly more silicon oxide in the free form than kaolin does, and SiO_2 in molding mixtures is known to act as a grog component decreasing plasticity. Thus, in order to obtain sorbents based on zeolite NaA, it is advisable to use clay from the Malostupkinskoe deposit.

Clay contacting water rather soon disintegrates into particles whose size approaches that of colloid particles. At the same time, the minerals constituting natural clay, in additional to physical sorption, are capable of reacting with the dispersion medium, which is manifested, in particular, in dehydration of their surface [7]. Water molecules relatively easily penetrate the interlayer space of the main mineral, i.e., kaolinite. This results in hydraulic dispersion of particles. Furthermore, owing to the specified phenomena, kaolinite forms strong coagulation bonds. Zeolite particles do not disperse in water. Although zeolite absorbs water, water molecules are categorized as physically sorbed and their energy is lower than in the formation of coagulation contacts, which prevents the formation of a sufficiently strong coagulation structure. This is corroborated by the fact that zeolite in its pure form is not moldable by extrusion. Summarizing all the above, we can conclude that zeolite systems in molding mixtures play the role of grog additives.

Another method for controlling the rheological and structural-mechanical properties of molding mixtures is acid or alkali treatment of clay. Acid and alkali treatment modifies the chemical composition of clay, which affects the formation of coagulation bonds [4]. Acid treatment destroys the crystalline structure of argillaceous minerals by decreasing the content of sequioxides in their chemical composition and forming amorphous silica, which contributed to the formation of an extended surface. Alkali treatment is accompanied by incorporation of sodium into the structure of argillaceous materials and facilitates the formation of hydrated complexes, which increases the dispersion of particles and improves the hydrophilic properties of samples.

When Malostupkinskoe clay is modified with hydrochloric acid (Fig. 1 and Table 1), the share of plastic deformations decreases approximately 3.5 times due to the uniform increase in the share of fast elastic and elastic deformations. When samples are treated with alkali, plastic deformation decreases to a less extent: approximately 1.5 times. In this case approximately equal manifestation of all types of deformation is observed, with a slight prevalence of plastic deformation (approximately 40%). At the same time, acid and alkali treatment of clay extends its relaxation period 9 and 4 times, respectively.

Analyzing the rheological properties of samples subjected to acid and alkali treatment (Table 1), it can be stated that the strongest coagulation structure is registered in the clay treated with NaOH: 12.2 MW/m^3. The flow index of the molding mixture in this case decreases to 0.30. As for the sample subjected to acid treatment, the power spent on destroying its coagulation structure and the flow index vary to a much lesser extent: 4.5 MW/m^3 and 0.49, respectively. Consequently, it can be concluded that alkali treatment of clay improves the properties of molding mixtures and makes them more suitable for extruding sorbents with a complex profile.

In addition of zeolite NaA, we have investigated the behavior of molding mixtures based on zeolite NaY

TABLE 2

Material	Weight content, %				
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Malostupkinskoe clay	55.84	15.90	5.35	6.31	4.11
Kyshtymskoe kaolin*	46.40	32.05	0.30	0.30	0.30

* Besides, Kyshtymskoe kaolin contains 1.00% TiO_2.

($28Na_2O \cdot 28Al_2O_3 \cdot 136SiO_2 \cdot nH_2O$) and mordenite ($4Na_2O \cdot 4Al_2O_3 \cdot 40SiO_2 \cdot nH_2O$). According to the classification given in [1], these materials based on their acid resistance are ranked in the following series: mordenite → NaY → NaA. With respect to the $SiO_2 : Al_2O_3$ molar ratio, this series has the same order: mordenite (10.0 : 1.00) → NaY (4.6 : 1.0) → NaA (2.0 : 1.0), whereas the $Na_2O : (Al_2O_3 + SiO_2)$ molar ratio has the reverse order: NaA (1.0 : 3.0) → NaY (1.0 : 5.9) → mordenite (1.0 : 11.0). This is a significant factor, since the quantity of Na^+ cations in zeolite of a particular type affects the pH of the molding mixture. The larger is the number of Na^+ cations in zeolite, the higher is the pH of molding mixtures based on this zeolite.

Figure 3 shows the diagram of deformations in molding mixtures based on zeolites with 30% Malostupkinskoe clay and Kyshtymskoe kaolin. As the molar content of Na_2O grows, i.e., in the NaA → NaY → mordenite series the share of plastic deformations grows, both in molding mixtures with Malostupkinskoe clay and with Kyshtymskoe kaolin. This is due to the fact that a higher content of sodium in zeolite (and accordingly, a higher plasticity of the system) improves the plasticizing properties of natural aluminosilicates. Note that the use of kaolin makes it possible to obtain molding mixtures with a higher share of plastic deformation than the use of Malostupkinskoe clay additive.

The increased content of sodium ions in zeolites decrease the shear stress and the maximum plastic viscosity of molding mixtures (Table 3). At the same time, in using the kaolin additive, the shear stress varies insignificantly, whereas using clay it decreases by more than half. The similar effect is observed for the maximum plastic viscosity. Thus, when kaolin is used as the plasticizing additive, the maximum plastic viscosity in the mordenite → NaY → NaA zeolite series decreases about 3 times and with the clay additive — 10 times.

The decrease in the content of Na_2O in zeolites also leads to decreasing rated of propagation of plastic deformation and the growth in the period of relaxation of the molding mixture.

A decreasing content of Na_2O in zeolites also decreases the rate of plastic deformation and increases the relaxation period of the molding mixture. All the above regularities of parameters changing depending on the molar ratio of $Na_2O : (Al_2O_3 + SiO_2)$ and the aluminosilicate additive hold in this case as well. Consequently, the most suitable for extrusion molding are mixtures using zeolite NaA.

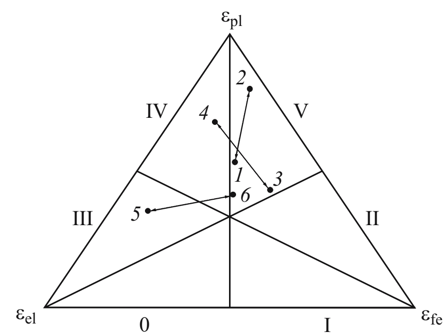

Fig. 3. Diagram of deformations in molding mixtures based on zeolite NaA and natural aluminosilicates: *1*, *3*, *5*) 70% Kyshtymskoe kaolin; *2*, *4*, *6*) 70% Malostupkinskoe clay. Zeolites: *1*, *2*) NaA, *3*, *4*) NaY; *5*, *6*) mordenite.

Thus, the new approach to the production of complex-profiled thin-walled sorbents based on zeolite NaA for sewage purification from metal cations has been studied. It is proposed to use natural aluminosilicates, in particular, clay from the Malostupkinskoe deposit and kaolin from the Kyshtymskoe deposit as binders in the production of sorbents. The following regularity has been established: the growth in the quantity of zeolite NaA in molding mixtures is accompanied by their decreasing plasticity due to a sharp increase in the share of elastic deformation, consequently, the moldability of mixtures is impaired.

The replacement of the binder (using kaolin instead of clay) leads to an excessive development of plastic deformations, which causes the emergence of defects in the course of extrusion.

It is established that treating clay with sodium hydroxide leads to hydraulic dispersion, which increases the specific surface area and makes molding mixtures more suitable for extrusion molding, whereas acid modifying destroys the crystalline structure of the aluminosilicate.

It is established that the most moldable are mixtures prepared with zeolite NaA.

Mixtures based on zeolite NaA and clay from the Malostupkinskoe deposit taken in the weight ratio of 1 : 1 can be

TABLE 3

Sample*	Zeolite type	30% aluminosilicate additive	Shear stress, kPa	Maximum plastic viscosity, 10^8 Pa · sec	Plasticity, 10^{-6} sec^{-1}	Relaxation period, sec
1	NaA	Kyshtymskoe kaolin	58.1	36.4	16.0	250
2		Malostupkinskoe clay	11.6	10.8	7.5	80
3	NaY	Kyshtymskoe kaolin	63.9	54.8	11.7	500
4		Malostupkinskoe clay	16.9	29.9	5.6	1500
5	Mordenite	Kyshtymskoe kaolin	64.4	94.8	1.5	1500
6		Malostupkinskoe clay	25.0	110.9	2.3	2000

* Numbers of samples correspond to those shown in Fig. 3.

recommended to produce extruded sorbents. It is advisable to preliminary modify clay with 1M NaOH solution.

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